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A systematic study of the structure of weakly bound complexes of hydrogen fluoride has been accomplished. This research provides a broad account of the interaction of hydrogen fluoride with a variety of laser components and atmospheric constituents. Precision structures are now available for the species ArHF, CO_2HF, N_2OHF and SCOHF as a result of the present research program. In addition, precision structures have been obtained for $ArCO_2$

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and ArN_2O.

This research provides the basic information necessary for reliable modelling of intermolecular forces between HF and Ar, CO_2, N_2O and OCS as well as between Ar and CO_2 and N_2O. Thus a more reliable understanding of relaxation processes in molecular gas lasers is now feasible. In addition the nature of weak interactions of atmospheric constituents has been explored with some of the above system (CO_2Ar) and species such as BF_3N_2 $COBF_3$ and $ArBF_3$. Considerable progress has been made in studying the rotational spectrum of $(CO)_2$. This species is sufficiently polar to permit high resolution rotational spectroscopy. It is of close relation to the atmospherically important system $(N_2)_2$.

Finally in all of the above systems precise measurement of electrical distortions that occur in weak bond formation were made. In attempting to model transmission of the electromagnetic spectrum in the atmsophere, it is essential to have a precise understanding of the electric dipole properties of atmospheric constituents. The present research has provided this information.

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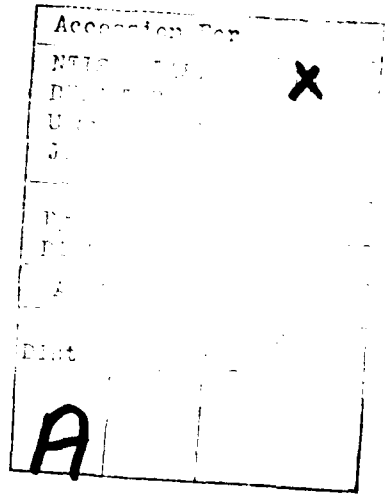
AFOSR-TR- 82-0661

FINAL REPORT

SPECTROSCOPIC DETERMINATION OF INTERMOLECULAR POTENTIALS OF GAS LASER COMPONENTS & OF MAJOR ATMOSPHERIC CONSTITUENTS

WILLIAM KLEMPERER

AFOSR-77-3269



HARVARD UNIVERSITY
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CAMBRIDGE, MA 02138

1982

FINAL REPORT

There has been a dramatic change in the depth and clarity of our understanding of intermolecular forces as a result of precision spectroscopic studies of molecular dimers. A major portion of the present research has been the study of hydrogen fluoride complexes. As a result of the present research program and other research programs, precise structures for approximately 20 molecular complexes of hydrogen fluoride are now known. It is worth noting that this development is relatively recent. For these species precise knowledge of the equilibrium geometry now exist as a result of rotational spectroscopy.

The complexes of hydrogen fluoride provide a means of understanding the interactions that occur in the important hydrogen fluoride laser. In the present program we have measured the structure of the complex of argon and hydrogen fluoride by means of radiofrequency and microwave spectroscopy. The average structure of the lowest vibrational state of ArHF has an argon hydrogen distance of 2.6304A and an ArHF angle of 138.8°. The structure of ArDF has an argon deuterium separation of 2.6256A and angle 147.0°. The estimated stretching vibration frequency of ArHF is 42.5 cm^{-1} and a bending frequency of 80 cm^{-1}. For ArDF the stretching frequency is estimated to be 45.6 cm^{-1} and the bending frequency is estimated to be 66 cm^{-1}. The electric dipole moments of the species are ArHF μ = 1.335 D, ArDF μ = 1.677 D for the ground vibrational states. There is no indication of distortion of the hydrogen fluoride bond in the complex. The equilibrium structure of ArHF is most likely linear. The complete publication provides details of the charge distribution.

The structure of more strongly bonded complexes of hydrogen fluoride are of considerable importance. The importance of the CO_2 gas laser and the nature of energy transfer in the HF-CO_2 system led to the study of the complex of hydrogen fluoride and carbon dioxide. The results are quite surprising. The observed structure of the system is OCOHF with an estimated linear equilibrium geometry. The system carbonyl sulfide hydrogen was also studied and a similar linear structure. The structure is SCO HF. The

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O...H bond length is similar in both species namely 1.91 A in the CO_2 complex and 1.94 in the OCS complex.

The bond stretching force constant for both species is quite similar namely 2.1×10^{-2} mdyne/A° in CO_2HF and 2.8×10^{-2} mdyn/A° in SCOHF. Clearly the most surprising result of this research is the linearity of the hydrogen bond. This is certainly not anticipated from the usual chemical pictures of the lone pair distribution in CO_2. It is, however, in reasonable accord with the charge distribution required by the large, negative quadrupole moment of CO_2. The charge distribution of the complex is appreciably altered from that of the functive units. The moment of the complex is about .6D greater in CO_2HF than the value of HF and about .8D greater than the vector seen of moments in SCOHF. It is clear that an appreciable electron rearrangement occurs even in weak bonding.

The reliable estimation of charge distortion that occurs in bonding was further pursued in the measurement and analysis of the deuterium quadrupole coupling constant. While the details are given in the published paper, it may be summarized showing that a change of approximately 3% occurs in the field gradient at the deuterium nucleus due to formation of the weak bond.

The structural results for the binary complex of hydrogen fluoride and carbon dioxide (together with the confirming study of HF and OCS) besides having an intrinsic value for the understanding of the interactions in this system provide a reference point for related structural studies. The structural study of a number of complexes of CO_2 by molecular beam rotational spectroscopy can be inhibited by the small electric dipole moment. It was for this and a number of related reasons that studies of nitrous oxide, N_2O, with hydrogen fluoride were made. N_2O is isoelectronic with CO_2 and appears to be quite similar in physical and molecular properties. It is similar in lasing properties to CO_2, although clearly not as important. It is a minor atmospheric component, though due to its possible photoactivated reactivity, has been at times regarded as important. The results of our structural study was quite surprising. The structure of the complex of N_2O and HF is strikingly different from that of CO_2

and HF. The structure of N_2O has a similar O...H distance namely 1.94A°, however, the geometric orientation of the two units is very non-linear. The system appears to be planar with a heavy atom angular arrangement N-O-F of 133°. The importance of this result lead us to measure precision spectra for a number of isotopic species. The results are:

	$^{14}N_2O$-HF	$^{15}N_2O$-HF	$^{14}N_2O$-DF	$^{15}N_2O$-DF
A(MHz)	26328.5(3)	25773.02(5)	26004.1(2)	25456.46(8)
B(MHz)	2718.6(10)	2646.57(4)	2699.7(1)	2626.68(6)
C(MHz)	2441.0(10)	2377.91(4)	2423.5(1)	2360.47(6)
μ_a(D)	2.069(4)		2.125(6)	
μ_b(D)	0.69(1)		0.63(2)	
Rc.m.(Å)	3.4635(3)	3.4825(3)	3.4140(3)	3.4262(3)

It is clear from these results that it will not be possible to model the interactions of N_2O either in the atmosphere or in a lasing medium simply in terms of related interactions of the more common CO_2.

The structure of complexes of CO_2 and N_2O with argon are extremely similar. The structures are "Tee" shaped. In the case of $ArCO_2$ the equilibruim geometry is a symmetric "Tee" with argon carbon weak bond length of 3.49Å. The electric diple moment is 0.0679D. It appears likely to us that other complexes of carbon dioxide likely to be of abundance in the atmosphere will in general have larger dipole moments. The likelihood is that these complexes, in particular N_2CO_2, can have a significant effect on the transmission characteristics of the atmosphere. The results for the $ArCO_2$ complex together with the studies of $ArBF_3$ and N_2BF_3 discussed below provide the only available precision data for electrical properties from which estimates of properties of substances such as N_2CO_2 can be made.

The structure of the complex of argon and nitrous oxide is virtually identical to that of $ArCO_2$. The Ar N distance is 3.46 A°. The estimated equilibrium geometry has an Ar-N-0 angle of 87 $\pm$ 1.5°. The results of these studies provide estimates of the vibrational frequencies of both $ArCO_2$ and ArN_20 from analysis of centrifugal distortion. They are Ar CO_2 : $\omega_{stretch} = 37cm^{-1}$ $\omega_{bend} = 39cm^{-1}$; Ar N_20 $\omega_{stretch} = 39cm^{-1}$ $\omega_{bend} = 45cm^{-1}$.

From analysis of these data it is clear that simple atom-atom intermolecular potentials give a poor representation of the interaction.

The study of the species $ArBF_3$, N_2BF_3 and $OCBF_3$ provides a comparison base for the expected interactions of argon, nitrogen and carbon monoxide in general. The species are produced by supersonic expansion. Their microwave spectra are recorded by molecular beam electric resonance spectroscopy. All three species are symmetric rotors. For $ArBF_3$ the Ar-B bond length is 3.325(10)Å, the stretching vibration frequency is 4-(2)cm^{-1}, and the electric dipole moment is 0.176(2)D. For BF_3CO the B-C bond length is 2.886(5)Å, the stretching vibration frequency is 65(8) cm^{-1}, and the electric dipole moment is 0.592(1)D. For N_2BF_3 the B-N bond length is 2.875(20)Å and the electric dipole moment is 0.35(2)D. The three species appear to be weakly bound charge transfer complexes.

There is a considerable similarity between the interactions of BF_3 and those of SO_3. In other work we have shown that the atmospherically important species SO_3 can be viewed as interacting more strongly than BF_3. In particular the electric dipole moments produced from the non polar species Ar and nitrogen are approximately 50% greater in SO_3 complexes than in the related BF_3 complex. The stretching force constants appear also to be a factor of two greater in the SO_3 complex.

It is clear that BF_3 is an extremely useful substance on which to base estimates of the interactions likely to occur in the SO_3 system. The wealth of classical complex chemistry available for BF_3 which now may be linked by these studies to weak interactions makes this system unique.

The comparison of Ar, N_2 and CO shows that in weak interactions the strenth of bonding goes, as expected, chemically, Ar < N_2 < CO. It appears likely that modelling of N_2 interactions on the basis of known argon interactions can be achieved. In an attempt to gain a better understanding of the CO (and therefore N_2) system the dimeric species $(CO)_2$ was studied. Five microwave transitions of $(CO)_2$ were observed. They are at

1.45797 GHz
16.07864 GHz
16.07905 GHz
16.07943 GHz
16.07983 GHz

It appears likely that $(CO)_2$ is a highly non-rigid molecule. At this time the structure of this species is not determined. Clearly the relevence of the structure of $(CO)_2$ to that of $(N_2)_2$ is high.

This research provides a precision basis for the development of our understanding of intermolecular interactions. It is unique in providing in addition to the geometric structures of complexes, precision (10^{-3} -10^{-4}) values of electric dipole moments. It establishes that for weak interactions, especially among molecules, the dipole moments produced by the interaction of non polar species can be much different from that obtained by elementary electrostatic modelling. It appears likely that reliable modelling of the atmospheric opacity the electromagnetic spectrum will require detailed measurements of the electrical and potential parameters of complexes.


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